Does Linseed Oil Contain Conjugated Double Bonds?

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ALTHOUGH it is not expected that readers not trained in organic chemistry will be able to understand the technical chemistry involved in this discussion, this article is printed in this Bulletin to illustrate the kind of chemical facts which must accompany our efforts at improving the quality of linseed oil through plant breeding. The chemist and the plant breeder must work hand-in-hand. The experiments which the authors report in this brief article lead to a negative conclusion; that is, the answer to the question which they raise in the title of this article is, as far as present evidence is concerned, linseed oils produced from flax do not contain conjugated bonds. It would appear, therefore, that the drying oil industry, which seeks the superior drying power which comes from the existence of conjugated double bonds in the oil, must continue to supply its needs from domestic and imported tung (Chinawood oil), imported oiticica oil, by dehydration of castor oil or possibly by subjecting other oils to chemical processes so as to create "tailor-made" oils.

This article also illustrates the fact that scientists in different parts of the United States cooperate. The North Dakota Station did not own the optical apparatus necessary to examine the capacity of oils to absorb light. Through the courtesy of the Purdue Station, which had the necessary apparatus, these determinations were made for this Station.

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Drying oils are characterized by greater unsaturation (the presence of more double bonds) than are non-drying oils. Oils differ not only by the total number of double bonds in the fatty acids, but also by the distribution of double bonds. When the double bonds are separated by a methylene carbon atom, -CH=CH-CH_2-CH=CH-, they are designated as isolated, but when at adjacent carbon atoms, -CH=CH-CH=CH-, they are called conjugated.

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The drying properties of the better known drying oils from vegetable sources depend for the most part upon the unsaturated fatty acids linoleic and linolenic, which contain two and three isolated double bonds. Linseed and perilla oils, as well as the slower drying oils such as safflower, hempseed, sunflower and soybean, contain varying amounts of these unsaturated acids along with oleic and saturated (non-drying) fatty acids.

Tung and oiticica oils, on the other hand, possess conjugated double bonds. These oils dry faster than oils with isolated double bonds, and the films produced are more resistant to water and caustic reagents. These oils are especially useful as varnish oils.

Oils with conjugated double bonds are in great demand and bring a much higher price than non-conjugated oils. Tung oil has been the chief conjugated oil used in drying industries, but it is now difficult to obtain because China is the chief producer. Domestic production is very small. Oiticica is imported from Brazil, but owing to troublesome physical characteristics industrial utilization has been small.

The requirements of the paint and varnish industries have challenged chemists to make from available materials suitable substitutes for products no longer available. Dehydration of castor oil gives a conjugated oil and the product is now in commercial production. When heated with alkaline reagents, oils such as linseed or soybean give conjugated fatty acids. The objection to this method is that saponification results and the fatty acids must be esterified with glycerol to convert back to an oil. Some success has been achieved in rearranging the double bonds to conjugated systems without saponification. Esterification of unsaturated fatty acids with higher (polyhydroxy) alcohols or by replacement of some of the fatty acids with specific reagents gives products with excellent drying properties.

Many "tailor made oils" are excellent products, but for the most part production costs are too great to permit extensive use. The drying oil industries want a conjugated oil produced by seed grown in this country. Representatives of industry raise the question: Is it possible to grow flax which will contain oil with conjugated double bonds?

We have, therefore, examined a number of linseed oils from several varieties to determine whether or not conjugated systems are naturally present in them.

Conjugation in oils can be measured by the difference in addition of halogens to the double bonds (1, 2) and by light absorption in the ultraviolet (3). Wijs iodine solution adds quantitatively to isolated double bonds in oils, but not to conjugated double bonds. Woburn iodine solution (1, 2), however, adds quantitatively to both isolated and conjugated double bonds. From the difference in addition by the use of different halogen solutions, von Mikusch and Frazier (1, 2) have attempted to measure conjugation in conjugated fatty acids of linseed and soybean oils as well as in unaltered oils.

Wijs and Woburn iodine numbers were determined in this laboratory on several samples of flaxseed grown at widely separated locations in North America. The results are shown in Table 1.

It may seem surprising that in most cases the Wijs values are slightly higher than the Woburn values, inasmuch as the latter reagent is reported to saturate all double bonds. Similar results were obtained by von Mikusch and Frazier (2) on a single linseed oil

Table 1—Wijs and Woburn Iodine Numbers of Linseed Oil Samples.

Oil No.		Location grown	Year grown	Iodine number: Woburn	Iodine number: Wijs	Difference: Woburn minus Wijs
1	Bison	Bozeman, Mont.	1935	176.4	177.0	—0.6
2	"	Saskatoon, Sask.	1935	184.8	187.0	—2.2
3	"	Newell, S. D.	1935	170.1	171.0	—0.9
4	"	Fargo, N. D.	1939	167.3	168.3	—1.0
5	"	Fargo, N. D.	1941	154.5	156.8	—2.3
6	Redwing	Bozeman, Mont.	1935	186.2	187.6	—1.4
7	"	Union, Ore.	1935	191.1	190.9	+0.2
8	"	Newell, S. D.	1935	180.1	180.5	—0.4
9	"	Fargo, N. D.	1939	181.8	182.3	—0.5
10	Rio	Bozeman, Mont.	1935	176.2	177.4	—1.2
11	"	Moccasin, Mont.	1936	160.1	161.9	—1.8
12	"	Union, Ore.	1935	177.0	178.4	—1.4
13	"	Newell, S. D.	1935	171.2	171.9	—0.7
14	"	Fargo, N. D.	1939	165.9	165.2	+0.7
15	Linota	Bozeman, Mont.	1935	188.2	188.2	0.0
16	"	Moccasin, Mont.	1936	179.7	179.2	+0.5
17	"	Union, Ore.	1935	191.4	192.3	—0.9
18	"	Newell, S. D.	1935	180.7	181.3	—0.6
19	B. Golden	Fargo, N. D.	1935	179.9	180.0	—0.1
20	"	Fargo, N. D.	1941	169.9	169.0	+0.9
21	"	Fargo, N. D.	1939	178.8	179.4	—0.6
22	"	Fargo, N. D.	1942	191.5	191.7	—0.2
23	"	Fargo, N. D.	1942	194.7	196.3	—1.6
24	Buda	Edmonton, Alta.	1938	194.3	196.0	—1.7
25	Walsh	Edmonton, Alta.	1938	189.2	190.6	—1.4
26	Punjab	El Centro, Cal.	1934	187.8	186.1	+1.7
27	Abyssinian	Calingula, Cal.	1934	193.7	194.1	—0.4

sample unless the Woburn reagent was 0.4 N. We experienced difficulty in obtaining precise results with the Woburn method.

Many of the oils in Table 1 were from flaxseed grown several years ago (4) and the oils had been stored for more than a year in the laboratory. Results on oils obtained from the 1943 field trials comparing varieties on the Agronomy plots of this station are shown in Table 2.

With the exception of oils No. 44 and 45 all of the values obtained by the two methods appear to be within the limits expected from the precision of the analyses. These two oils show higher values by the Woburn method, which could be interpreted to indicate the presence of conjugated double bonds. The differences of 3.1 and 3.3 points indicate a relatively small proportion of conjugated bonds because with linseed oil fatty acids conjugated by alkaline reagents (1) the Woburn iodine number was as much as 30 points higher than the Wijs.

In order to definitely determine whether or not the two oils, No. 44 and 45, contain conjugated systems they were sent to the Agricultural Chemistry Department of Purdue University where their absorption in the ultraviolet was determined. Conjugated linoleic acid shows a maximum absorption at 2340A° (due to diene conjugation) and conjugated linolenic acid shows maximum absorption at 2340A° and at 2680A° (due to triene conjugation) (5).

Neither of the two oils showed light absorption at 2340A°. At approximately 2700A° there was a

Table 2—Wijs and Woburn Iodine Numbers of Linseed Oil Samples from the 1943 Agronomy Trials.

Oil No.	Variety	Iodine number: Woburn	Iodine number: Wijs	Difference: Woburn minus Wijs
28	Renew	184.1	184.3	—0.2
29	Buda	188.7	187.2	+1.5
30	Royal	178.8	179.6	—0.8
31	Biwing	189.8	189.1	+0.7
32	Bison	181.4	181.2	+0.2
33	Crystal	189.6	191.5	—1.9
34	Kota	188.9	188.4	+0.5
35	B 5585	190.0	189.7	+0.3
36	B 5128	183.2	183.4	—0.2
37	B. Golden	195.7	194.7	+1.0
38	B 5577	187.5	185.6	+1.9
39	C.I.976(R.557)	195.7	194.0	+1.7
40	C.I.977(R.522)	191.8	190.5	+1.3
41	Ns 3092	186.9	185.6	+1.3
42	Ns 3093	190.6	188.7	+1.9
43	Viking	196.6	194.7	+1.9
44	C.I. 1049	192.8	189.7	+3.1
45	C.I. 1069	189.7	186.4	+3.3
46	C.I. 1070	182.1	182.3	—0.2
47	C.I. 1073	190.9	191.8	—0.9
48	B 55	181.2	183.3	—2.1
49	B 147	183.1	182.2	+0.9
50	B 2695	186.7	186.5	+0.2
51	B 2760	185.2	185.3	—0.1
52	B 2786	180.8	180.7	+0.1
53	B 5593	187.2	187.9	—0.7

slight maximum, but the amount was no greater than found by Mitchell and Kraybill (3) in other linseed oils. The specific "alpha" (a numerical measure of light absorption) for each of the oils at 2680A° was less than 1/1000 the value for conjugated linolenic acid (5).

The discrepancy between the results by the Woburn method and spectroscopic method is diffifult to explain, but there appears to be no question regarding conjugated systems in the linseed oil samples. Linseed oils show slight absorption near that for triene conjugated systems but the absorption is so small that conjugation, if present, is infinitesimal. The data show that for all practical purposes linseed oils now produced do not contain conjugated systems.

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